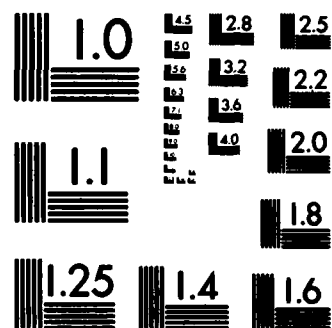


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Measurements of the partial pressures in the mercury-cadmium-tellurium system are indicated. The thermodynamic analysis of this system is briefly sketched. References to detailed accounts of these results are cited. There now exist sufficient data that this system is to a large extent thermodynamically characterized. Moreover, a thermodynamic model has been established that allows a quantitative reproduction of essentially all of what appears to be the reliable phase diagram, partial pressure, and general thermodynamic data.		

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Report 5
Properties of Mercury-Cadmium-Telluride Solid Solutions

Final Report
July 1, 1978-June 30, 1983

by
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I. RESEARCH OBJECTIVES

A) Thermodynamically characterize the Hg-Cd-Te system by determining the partial pressures of Hg, Cd, and Te_2 as a function of composition and temperature. In particular determine the partial pressures for Te-saturated and for metal (Hg-Cd)-saturated solid solutions of various x-values in the formula, $\text{Hg}_{1-x}\text{Cd}_x\text{Te(s)}$. The partial pressures will be determined by measuring the optical absorbance between 200 and 800 nm of the vapor phase coexisting with a liquid phase, or a solid solution phase, or a combination of two such condensed phases of known composition and temperature.

B) Combine the above experimental data with all other available, reliable, phase diagram and thermodynamic data and seek a simultaneous, quantitative, fit with a thermodynamic model.

II. STATUS OF THE RESEARCH EFFORT

The research objectives set forth have almost all been achieved. Since most of the results have already been written up and published, or accepted for publication, in the scientific literature, only a summary of these results will be given here. The full details are available in the references cited.

The details of our experimental system, the experiments necessary to obtain the partial pressures of Hg, Cd, and Te_2 from measurements of the optical absorbance of the vapor between 210 and 800 nm, and the partial pressures for both the Te-saturated and the metal (Hg-Cd)-saturated solid solution, $\text{Hg}_{.60}\text{Cd}_{.40}\text{Te(s)}$, have been given (1). These partial pressures were then measured for both Te-saturated and for metal-saturated $\text{Hg}_{1-x}\text{Cd}_x\text{Te(s)}$ for $x = 0.10$ and 0.20 and for Te-saturated $x = 0.58$, as well as for composi-

tions within the homogeneity range for these x -values (2). These experiments establish that the chemical potentials of the thermodynamic species, HgTe and CdTe, in the solid solutions are stoichiometric invariants i.e. independent of the Te to Hg + Cd atomic ratio, as expected theoretically (3). In effect numerical relations are established so that for a given temperature and x -value, the partial pressures of any two of the vapor species, Hg, Cd, and Te_2 , can be calculated if one is given. These experiments also yield the solidus temperatures for $x = 0.108$, 0.198 , and 0.41 in good agreement with values obtained by more conventional techniques. Moreover they showed that Hg is the predominant vapor species over the solid solutions and that at temperatures below 500°C that the partial pressure of Hg over the Te-saturated solid solutions is under 1 atm, thus indicating the feasibility of epitaxial growth of these solid solutions from Te-rich liquids below 500°C .

The basic thermodynamic equations fixing the liquidus surface of a solid solution such as $(\text{Hg}_{1-x}\text{Cd}_x)_y\text{Te}_{1-y}(\text{s})$, when y is confined to values close to unity, have been derived in a form independent of the thermodynamic model of the liquid phase (4). A number of previous analyses of phase diagrams could then be shown to have used incorrect starting equations. A widely used simplification of the associated solution model introduced by Jordan was then used to successfully fit the phase diagram and thermodynamic data for the HgTe-CdTe-Te subsystem but was also shown to be incapable of fitting the entire Hg-Cd-Te system (5). As a consequence, a more general associated solution model for the liquid phase was successfully employed to obtain a quantitative, simultaneous fit to the phase diagram and thermodynamic data for the entire Hg-Cd-Te system (6). This paper included an repetition and extension of our earlier measurements for the partial pressures over Te-saturated solid solutions with $x = 0.40$ and 0.58 . The

theoretical analyses in Ref. (6) used a value for the enthalpy of fusion of HgTe(s) obtained in measurements (7) of the partial pressures over Te-saturated HgTe(s) and over the 50 at % Te melt. These measurements in Ref. (7) also gave corrected values for the partial pressure of Te_2 over Te-saturated HgTe(s) at high temperatures.

The theoretical analysis given in Ref. (6) was then extended (8) and found to give liquidus isotherms and tie-lines in the Hg-rich corner between 360 and 500°C in good agreement with experiment. These data show the striking feature, reproduced by calculation, that the tie-lines tend to converge towards the Hg corner of the Hg-Cd-Te phase diagram so that almost pure CdTe(s) is grown from an almost pure Hg(l). Thus extraordinary composition control of the melt is required to grow a crystal of $\text{Hg}_{1-x}\text{Cd}_x\text{Te(s)}$ of a specified x-value. The theoretical analysis also gave the partial pressures of Hg required for metal-saturation of $\text{Hg}_{1-x}\text{Cd}_x\text{Te(s)}$ between 250 and 300°C and showed these to be very close to the vapor pressure of Hg.

Concurrently with the application of the associated solution model to the Hg-Cd-Te system described above, the same general model was successfully applied to an analysis of the phase diagram and thermodynamic properties of the Ga-In-Sb system (9). The situation is simpler than for the Hg-Cd-Te system in that more of the interaction parameters for the liquid phase systems can be set equal to zero.

An extensive report (10) of the properties of the associated solution model and of its application to the Ga-In-Sb and Hg-Cd-Te systems has been prepared and should soon appear in print. This report includes more experimental data for the Hg-Cd-Te system and corresponding calculated values obtained from our model. In particular, the liquidus surface in the Hg-Cd-Te

system forms a ridge, which although terminating at the HgTe and CdTe compositions, falls outside the HgTe-CdTe pseudobinary section and towards the Hg-Cd binary for intermediate x -values. Recent liquidus temperatures obtained by others using differential thermal analysis are reproduced within 10°C by our model. Moreover, total pressure measurements obtained earlier by Steininger can now be accounted for, although some of these can be plausibly concluded to be in error in that they were assumed to be for a liquid phase rather than a liquid-solid two phase mixture. Essentially all of the extensive phase diagram and partial pressure data for the Hg-Cd-Te system can be quantitatively reproduced with a single set of liquid phase model parameters and input thermodynamic quantities for the binary compounds, HgTe and CdTe.

We had earlier (11) given a defect chemistry analysis of $\text{Hg}_{.60}\text{Cd}_{.40}\text{Te}(s)$ based upon the saturation experiments of Schmit and Stelzer. More recently Vydyanath and his coworkers have obtained more extensive carrier concentration - Hg pressure - temperature data for $x = 0.20$ and 0.40 and given a defect chemistry analysis. We have generalized (12) this analysis for $x = 0.20$, 0.40 , and 1.0 using values for the intrinsic carrier concentration at high temperature calculated from the band structure parameters rather than obtained as arbitrarily disposable parameters of a fitting process. In so doing we found and used an exact expression for the density of states in the Kane conduction band, rather than the approximate expressions previously used. The results of $x = 0.20$ and 0.40 are good, but not quite as good as we believe they should be. Whether this is to be attributed to error in the experimental values for the carrier concentrations, which were obtained on quenched samples, or in the high temperature band structure is uncertain at the moment.

The defect chemistry analysis briefly described above and given in Ref. (12) was one of our objectives for the final nine months of this Grant. Another objective was to attempt to improve the accuracy with which the partial pressure of Cd is measured. The optical absorbance of the vapor over a number of Hg-Cd amalgams was measured and the extensive thermodynamic data on the Hg-Cd system critically reviewed. As a result the quantitative relationship between the integrated absorption of the Cd peaks and the Cd partial pressures has been changed slightly. The previously obtained Cd pressures have then been recalculated using this new relationship. The largest corrections are in the lowest pressure range where the new values for the Cd pressure are about twice as large as the old values. These results, as well as the partial pressures over the Te-saturated $\text{Hg}_{1-x}\text{Cd}_x\text{Te(s)}$ for $x = 0.70$ and 0.95 , which have not been published previously, are being incorporated in the Dissertation of Pok-Kai Liao (13).

Most recently we have repeated and extended our measurements of the optical absorbance over pure Hg, pure Cd, and pure Zn samples. We have always used this type of measurement as a basis for obtaining partial pressures. However, a theoretical analysis of the line shape based on the recent literature and using the statistical broadening theory has allowed a determination of the oscillator strengths of the Cd 228 nm line and the Zn-217 nm line. Moreover, the ground state pair-interaction potentials as a function of separation have been obtained for Hg-Hg, Cd-Cd, and for Zn-Zn as well as the pair interaction potentials for $\text{Hg}6^3\text{P}_1 - \text{Hg}6^1\text{S}_0$, $\text{Zn}4^1\text{P}_1 - \text{Zn}4^1\text{S}_0$, and for $\text{Cd}5^1\text{P}_1 - \text{Cd}5^1\text{S}_0$. We are in the process of writing up these results.

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13. "Further Thermodynamic Characterization of the Hg-Cd-Te System by Optical Absorbance of the Vapor Phase", Pok-Kai Liao. A Dissertation currently being written and to be submitted to the Graduate School of Marquette University, Milwaukee, WI as partial fulfillment of the requirements for a Ph.D. in Materials Science and Metallurgy.

III. PUBLICATIONS PLANNED

We plan to write up and submit for publication the results obtained on the vapor phase interaction of Hg, of Cd, and of Zn as described in the last paragraph of Section II.

IV. PERSONNEL

Robert F. Brebrick, Professor, Mechanical Engineering and principal investigator has been supported full time for 2 months each summer and 1/4 time during the academic year since July 1, 1978.

Dr. Ahmed Mubarek worked full time on the grant for one month, 8/1/78 to 9/1/78. Ahmed is now teaching at the University of Jordan.

Dr. Leszek Golonka worked full time on the grant as a research associate from 9/15/78 to 10/1/79. He then returned to his position as a professor in the Technical University, Institute of Electron Technology, Wroclaw, Poland. Dr. Maria Golonka worked 1/2 time on the grant from 4/1/79 to 7/1/79.

Tse Tung worked on the grant as a graduate student in the Material Science and Metallurgy Ph.D. program. He was supported full time throughout the year from July 1, 1978 to July 1, 1981. Since then he has been working as a research scientist at Martin Marietta Lab., Baltimore on the epitaxial growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te(s)}$. Mr. Tung passed his final doctoral examination in May, 1983.

Ching-Hua Su entered the program in Materials Science and Metallurgy in Jan. 1980. He was supported on the grant for 3 summer months in 1981 and 1982 and has been supported full time from Sept. 1, 1981 to date. Mr. Su is currently finishing the writing of his dissertation, "Defect Chemistry and Intrinsic Carrier Concentration for $\text{Hg}_{1-x}\text{Cd}_x\text{Te(s)}$ for $x = 0.20, 0.40,$ and 1.0 ". We anticipate that he will pass his final examination for the Ph.D. degree sometime in the summer of 1983.

Pok-Kai Liao entered the Materials Science and Metallurgy program at Marquette in June, 1980. He was supported on the grant for 3 summer months in 1981 and 1982 and by a University Fellowship during the academic year.

Mr. Yu Huang entered the program in Materials Science and Metallurgy at Marquette in Sept. 1980. He was supported under the grant for 3 summer months in 1981 and 1982. During the academic year he has served as a Teaching

Assistant until Sept. 1982 when he was awarded a Research Fellowship by the University. Mr. Huang will continue experimental and theoretical research as a candidate for the doctoral degree.

V. SUMMARY

The partial pressures of Hg, Cd, and Te_2 have been determined for a range of compositions and temperatures in the Hg-Cd-Te system. A few solidus temperatures in the HgTe-CdTe pseudobinary section and a few liquidus temperatures for Te-rich melts have also been determined. These have been used to obtain a number of thermodynamic quantities for the system. These data as well as the extensive phase diagram data have been simultaneously and quantitatively fit in a thermodynamically self-consistent way using an associated solution model for the liquidus phase. The vapor - $(\text{Hg}_{1-x}\text{Cd}_x)_{1-y}\text{Te}_y(\text{s})$, solid solution equilibrium i.e. the defect chemistry of the "pseudobinary" solid solution, has been analyzed in a more generalized and more satisfactory manner than before for $x = 0.20, 0.40$, and 1.00 . This analysis is based upon values of the high temperature intrinsic carrier concentration calculated from the band structure parameters using a simple, but hitherto overlooked, way of getting the exact density of states in a Kane conduction band. The results are given in detail in a number of papers which, with one exception, are already published or in press. These are cited here under references in Section II, Status of the Research Effort. The one exception is the dissertation cited in Ref. (13). This is now being written and should be completed and a copy in the Marquette Library by Sept. 1983.

